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PN - JP2000086822 A 20000328

TI - (A)

RESIN COMPOSITE MATERIAL

AB - (A)

PROBLEM TO BE SOLVED: To obtain a material excellent in thermostability and having flexible elasticity like a crosslinking rubber at an ordinary temperature by dispersing organic clay to at least one segment of thermoplastic elastomers of a blocked copolymer type composed of plural kinds of segments.

SOLUTION: An organic clay is preferably dispersed at 0.01-200 pts.wt. to 100 pts.wt. of an elastomer and at 0.1-300 pts.wt. to 100 pts.wt. of a component composed of a hard segment. In order to selectively disperse the organic clay in the hard segment, it uses preferably the elastomer composed of the hard one with or without a functional group or the soft segment having a polar functional group weaker than that of the hard one. The organic clay which has an ionic bond of an organic onium ion on the surface of the clay is specifically preferable. A resin composite material is obtained by kneading the organic clay and the elastomer by a twin-screw extruder.

FI - C08K3/34; C08K9/04; C08L21/00; C08L53/00

PA - (A)

TOYOTA CENTRAL RES &amp; DEV

IN - (A)

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AP - JP19980261375 19980916

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DT - I

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AN - 2000-298628 [26]

TI - Resin composite material for hose material, isolator, has organic clay dispersed in at least single segment of the block copolymer type thermoplastic elastomer which consists of many segments

AB - JP2000086822 NOVELTY - The resin composite material has organic clay (13) dispersed in at least one segment of the block copolymer type thermoplastic elastomer which consists of many segments (11, 12).

- USE - For hose material, isolator, motor vehicle interior and exterior cladding material.

- ADVANTAGE - The resin composite material has good heat resistance. The material has elasticity even at room temperature. The hardware segment increases the heat resistance of the resin composite and software segment increases the elasticity of the resin composite.

- DESCRIPTION OF DRAWING(S) - The figure shows the dispersion state of organic clay in resin composite material.

- Resin composite material 1

- Segments 11, 12

- Organic clay 13

- (Dwg.1/4)

IW - RESIN COMPOSITE MATERIAL HOSE MATERIAL ISOLATE ORGANIC CLAY DISPERSE SINGLE SEGMENT BLOCK COPOLYMER TYPE THERMOPLASTIC ELASTOMER CONSIST SEGMENT

PN - JP3374764B2 B2 20030210 DW200314 C08L21/00 008pp

- JP2000086822 A 20000328 DW200026 C08L21/00 008pp

IC - C08K3/34 ; C08K9/04 ; C08L21/00 ; C08L53/00

PA - (TOYW) TOYOTA CHUO KENKYUSHO KK

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PN - JP2000086822 A 20000328

TI - RESIN COMPOSITE MATERIAL

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- SOLUTION: An organic clay is preferably dispersed at 0.01-200 pts.wt. to 100 pts.wt. of an elastomer and at 0.1-300 pts.wt. to 100 pts.wt. of a component composed of a hard segment. In order to selectively disperse the organic clay in the hard segment, it uses preferably the elastomer composed of the hard one with or without a functional group or the soft segment having a polar functional group weaker than that of the hard one. The organic clay which has an ionic bond of an organic onium ion on the surface of the clay is specifically preferable. A resin composite material is obtained by kneading the organic clay and the elastomer by a twin-screw extruder.
- I - C08L21/00 ; C08K3/34 ; C08K9/04 ; C08L53/00
- PA - TOYOTA CENTRAL RES & DEV LAB INC
- IN - HASEGAWA NAOIKI; OKAMOTO HIROTAKA; USUKI ARIMITSU
- ABD - 20000922
- ABV - 200006
- AP - JP19980261375 19980916
- PD - 2000-03-28

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3. In the drawings, any words are not translated.

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## DETAILED DESCRIPTION

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the resin composite material which consists of thermoplastic elastomer and organic-ized clay.

[0002]

[Description of the Prior Art] Conventionally, the block-copolymer type thermoplastic elastomer 91 which consists of a hard segment 11 and a soft segment 12 has a large elastic modulus in order to take the condition that separation in a micron - submicron unit occurred (microfacies isolation construction), as shown in drawing 4 (a), and demonstrating the bridge formation rubber-engine performance is known.

[0003] It is because, as for this, block-copolymer type thermoplastic elastomer 91 consists of a hard segment 11 and a soft segment 12 (refer to drawing 2 mentioned later), a hard segment 11 has a functional group with a strong polarity, and a soft segment 12 does not have a polarity or it has the polar weak functional group.

[0004] Each combines the strong polar hard segment 11 firmly, the same structure and same role as the point constructing a bridge in bridge formation rubber will be played, and each hardly combines the soft segment 12 without a polarity (or it has a weak polarity). This structure bears a strong resemblance to the bridge formation rubber in the condition that between rubber molecules was combined at the point constructing a bridge. Therefore, such block-copolymer type thermoplastic elastomer 91 has the engine performance similar to common bridge formation rubber. And since it has the same moldability as the usual elastomer, it is greatly useful as various spring materials excellent in the moldability.

[0005] However, the problem that thermal resistance is low is known by the above-mentioned block-copolymer type thermoplastic elastomer 91. This is because association between the hard segments 11 in an elevated temperature [ be / the above-mentioned hard segment 11 / thermoplasticity ] becomes weak. When a hard segment 11 consists of styrene, an elastic modulus will fall at 70-80 degrees C, and resiliency like bridge formation rubber will be lost. Moreover, when a hard segment 11 consists of an amide or ester, an elastic modulus will fall at 100-150 degrees C, and resiliency will be lost.

[0006] In order to solve this problem, as conventionally shown in drawing 4 (b), the quantity of a hard segment 11 was increased, and the attempt which aims at heat-resistant improvement was made by making with the block-copolymer type thermoplastic elastomer 92 which increased the number and magnitude of the part which functions as a point constructing a bridge.

[0007]

[Problem(s) to be Solved] However, the degree of hardness in ordinary temperature rose, and the hard segment had a possibility that pliant resiliency like bridge formation rubber may be lost from block-copolymer type thermoplastic elastomer, in order that the amount of a soft segment might decrease relatively, if the quantity of a hard segment was increased in vain, since it is also a part with a high degree of hardness (refer to drawing 3 mentioned later).

[0008] This invention was made in view of this conventional trouble, is excellent in thermal resistance, and tends to offer the resin composite material which has pliant resiliency like bridge formation rubber also in ordinary temperature.

[0009]

[Means for Solving the Problem] The resin composite material characterized by organic-ized clay distributing to at least one kind of segment of block-copolymer type thermoplastic elastomer which consists of two or more kinds of segments has invention according to claim 1.

[0010] Whenever the block-copolymer type thermoplastic elastomer concerning this invention is shown in drawing 2 mentioned later, it comes, and it consists of polymers which consist of two or more kinds of segments, and each segment forms the microfacies isolation construction-separated in the field of a micron - submicron unit.

[0011] The above-mentioned organic-ized clay is distributed to the phase which consisted of at least one kind of segments of microfascies isolation construction. The phase which organic-ized clay distributes becomes settled with the compatibility of organic-ized clay and the molecule chain of the segment which forms each phase, and it is easy to distribute the above-mentioned organic-ized clay to polar high phases, such as a polyamide, polyurethane, poly urea, polyester, and polystyrene. In addition, even if a part of organic-ized clay is distributing to other phases, the effectiveness of this invention can be acquired.

[0012] It is desirable for the above-mentioned organic-ized clay to serve as particle size of 1 micrometer or less, and to distribute to the above-mentioned elastomer. Thereby, the effectiveness of this invention can be acquired certainly. Moreover, in case the above-mentioned organic-ized clay distributes to the above-mentioned segment, it is desirable that the segment (or polymer which constitutes this segment) has intercalated between the layers of the above-mentioned organic-ized clay.

[0013] The above-mentioned organic-ized clay is the matter with the layer structure. The above-mentioned segment entered between a certain layer which constitutes this organic-ized clay, and other layers, and the above-mentioned intercalation has pointed out the condition that the distance between layers of organic-ized clay became large rather than origin. In addition, this condition can be checked by using an X diffraction. When such intercalation arises, the interface of the front face of organic-ized clay and a segment becomes large. Therefore, a segment will be more strongly restrained by organic-ized clay. Therefore, association between segments can be strengthened more.

[0014] Moreover, it is desirable that 10A or more of distance between layers of organic-ized clay spreads rather than the original condition at least by the above-mentioned intercalation. It is desirable that 30 moreA or more spreads. Thereby, the effectiveness of this invention can be acquired more certainly. In addition, it is still more desirable that 100A or more of distance between layers spreads. Since the rate of the segment restrained by organic-ized clay when the distance between layers spreads increases, it is because association between segments becomes stronger.

[0015] Moreover, in case the above-mentioned organic-ized clay distributes to the above-mentioned segment, as for things, it is desirable that the layer structure of organic-ized clay disappears, each class turns into a monolayer, and it is in the condition of having carried out molecular dispersion to the segment. Since organic-ized clay can distribute to homogeneity to a segment by becoming a monolayer more, the rate of the segment restrained by organic-ized clay becomes the largest. Thereby, the effectiveness of this invention can be acquired more certainly. In addition, while all the organic-ized clay became a monolayer, it did not need to distribute to a segment and about several layers had changed into the laminating condition, you may exist.

[0016] Next, it explains per operation of this invention. The block-copolymer type thermoplastic elastomer which constitutes the resin composite material of this invention consists of two or more kinds of segments, and organic-ized clay is distributing it to at least one kind of these segments. In the segment which organic-ized clay distributed, in order that organic-ized clay may restrain a segment (refer to drawing 1 mentioned later), between segments will be combined by the strong force. In the segment which organic-ized clay is not distributing, between segments will be in the condition of having hardly joined together.

[0017] Since the segment combined by this organic-ized clay forms the same structure as the point in bridge formation rubber constructing a bridge, the resin composite material of this invention can obtain pliant resiliency like common rubber in ordinary temperature (refer to drawing 3 mentioned later). And the constraint by organic-ized clay cannot be easily influenced of heat. Therefore, a resin composite material excellent in thermal resistance can be obtained (refer to the example of an operation gestalt).

[0018] As mentioned above, according to this invention, it excels in thermal resistance and the resin composite material which has pliant resiliency like bridge formation rubber also in ordinary temperature can be offered.

[0019] Moreover, as mentioned above, an elastic modulus cannot fall easily due to an elevated temperature, and the resin composite material concerning this invention has the resiliency which resembled bridge formation rubber also in the elevated temperature. From this, the resin composite material of this invention can improve the creep property in an elevated temperature.

[0020] Next, the block-copolymer thermoplastic elastomer which constitutes the resin constituent of this example is explained. A block copolymer is a polymer which has the segment which consists of two or more different molecule chains into 1 molecule. Although the so-called AB mold, the ABA mold, and the ABC mold were illustrated to drawing 2 (a), (b), and (c), it is not limited to these. In addition, in this drawing, Segment A, Segment B, and Segment C are chains different, respectively.

[0021] It illustrates below about the polymer kind used as the segment which constitutes the above-mentioned block copolymer. For example, a polyamide, polyurethane, poly urea, poly car baud NETO, polyacetal, polyester, polyarylate, polyphenylene ether, polyphenylene sulfide, polyethylene, polypropylene, polybutene, the poly pentene, Ethylene propylene rubber, an ethylene-butene copolymer, polybutadiene, polyisoprene,

hydrogenation polybutadiene, hydrogenation polyisoprene, ethylene, a propylene, a diene copolymer, an ethylene-butene-diene copolymer, isobutylene isoprene rubber, polystyrene, Fluorine system polymers, such as a styrene-butadiene copolymer, a styrene-hydrogenation butadiene copolymer, a polyether, the poly amine, the poly ketone, poly phthalamide, polyether nitril, polybenzimidazole, polyimide, poly carbodiimide, and Pori 4 fluorination ethylene, Acrylic polymers, such as silicone system polymers, such as polyamidoimide, polyether imide, a liquid crystal polymer, polysilane, and a polysiloxane, and PMMA, etc. are mentioned.

[0022] Moreover, as an elastomer of marketing usable as the above-mentioned block copolymerization type thermoplastic elastomer, a tough tech (Asahi Chemical), Hytrel (Du Pont-Toray), pel Puren (Toyobo), GURIRAKKUSU (JSR), PEBAKKUSU (Toray Industries), a die amide (die cel Huels), the estrane (the Takeda HADISSHU urethane industry), etc. are mentioned.

[0023] As the above-mentioned block-copolymer thermoplastic elastomer, it is desirable that number average molecular weight is 5,000-10,000,000. When molecular weight is larger than 10,000,000, there is a possibility that the workability of resin composite material may fall. On the other hand, when molecular weight is less than 5,000, there is a possibility that the mechanical physical properties of resin composite may fall. In addition, as for the value of the minimum of the above-mentioned number average molecular weight, being referred to as 10,000 is more desirable.

[0024] The above-mentioned organic-ized clay is explained below. The above-mentioned organic-ized clay processes clay (clay mineral) by the organic-ized agent, and shows the clay which adsorbs and/or combined the organic substance with the front face. As clay, the various matter of smectite groups, such as kaolinite groups, such as a kaolinite and halloysite, a montmorillonite, beidellite, saponite, hectorite, and a mica, and a vermiculite group can be mentioned here, for example. Moreover, synthetic compounds [ like the fluorination mica of bloating tendency ] whose thing of the natural origin which is not limited to these or processing article of a natural product is also can be used. Moreover, it is desirable that one carbon number of the organic chain which constitutes this is four or more as the above-mentioned organic-ized agent.

[0025] Since hydrophobing of the clay cannot fully be carried out, in the case of less than three carbon number, the compatibility over a polymer is not enough, and, for this reason, there is a possibility that it may become impossible for organic-ized clay to fully distribute to a segment in it. In addition, unless degradation of resin composite material arises, the thing containing functional groups, such as a carboxylic acid, can also be used for the above-mentioned organic-ized agent. Moreover, the functional group contained in block-copolymer thermoplastic elastomer and a reaction may be possible for the functional group contained in the above-mentioned organic-ized agent. Moreover, the above-mentioned organic-ized agent may have branching structure and cyclic structure.

[0026] Moreover, in such organic-ized clay, especially a desirable thing is organic-ized clay made organic, when organic onium ion carries out ionic bond on the surface of clay. As this onium ion, the ammonium ion of the 1-4th class and phosphonium ion are desirable, for example.

[0027] An example of onium ion is listed below. For example, it can consider as butyl ammonium, hexyl ammonium, octyl ammonium, DESHIRU ammonium, dodecyl ammonium, octadecyl ammonium, butyl methylammonium, hexyl methylammonium, octyl methylammonium, DESHIRU methylammonium, dodecyl methylammonium, octadecyl methylammonium, etc.

[0028] Moreover, it can consider as butyldimethyl ammonium, pentyl dimethylammonium, hexyl dimethylammonium, heptyl dimethylammonium, octyl dimethylammonium, DESHIRU dimethylammonium, dodecyl dimethylammonium, octadecyl dimethylammonium, etc.

[0029] Moreover, it can consider as dibutyl ammonium, dihexyl ammonium, dioctyl ammonium, JIDESHIRU ammonium, didodecyl ammonium, dioctadecyl ammonium, etc. Moreover, it can consider as butyldimethyl ammonium, hexyl dimethylammonium, octyl dimethylammonium, DESHIRU dimethylammonium, dodecyl dimethylammonium, octadecyl dimethylammonium, etc.

[0030] Moreover, it can consider as tributyl ammonium, trihexyl ammonium, trioctyl ammonium, tridecyl ammonium, tridodecyl ammonium, trio KUTADE sill ammonium, etc. Moreover, it can consider as butyl trimethylammonium, hexyl trimethylammonium, octyl trimethylammonium, DESHIRU trimethylammonium, dodecyl trimethylammonium, octadecyl trimethylammonium, etc.

[0031] Moreover, it can consider as dibutyl dimethylammonium, dihexyl dimethylammonium, dioctyl dimethylammonium, JIDESHIRU dimethylammonium, didodecyl dimethylammonium, dioctadecyl dimethylammonium, etc. Moreover, it can consider as tetrabutylammonium, tetra-hexyl ammonium, tetra-octyl ammonium, tetradecyl ammonium, tetra-dodecyl ammonium, tetra-octadecyl ammonium, etc.

[0032] Moreover, it can consider as the ammonium salt of 12-amino dodecanoic acid, 18-amino octadecanoic acid, an aniline, a pyridine, and a pyrrole etc. Of course, it is not limited to each matter mentioned above.

[0033] Moreover, the ion obtained from the following salts can be mentioned as phosphonium ion. A tetraethyl

phosphonium star's picture, triethyl benzyl phosphonium chloride, a tetra-n-butyl phosphonium star's picture, the tetra-n-butyl phosphonium n, n-diethyl phosphorodithioate, tetra-n-butyl phosphonium benzo TORIAZORETO, Tori n-butyl methyl phosphonium iodide, a Tori n-butyl octyl HONIU star's picture, a Tori n-butyl hexadecyl phosphonium star's picture, a Tori n-butyl aryl phosphonium star's picture, Tori n-butyl benzoyl phosphonium chloride, A Tori n-octyl ethyl phosphonium star's picture and a tetrakis (HIRODOKISHI methyl) phosphonium are mentioned.

[0034] Moreover, as for the amount of the organic-ized clay to block-copolymer type thermoplastic elastomer, in the resin composite material of this invention, it is desirable that organic-ized clay considers as the 0.01 - 200 weight section to the elastomer 100 weight section. Thereby, thermal resistance can be raised and a creep property can be raised.

[0035] When organic-ized clay is under the 0.01 weight section, there are [ to restrain between segments enough but ] too few amounts of organic-ized clay, and there is a possibility that the effectiveness of this invention may no longer be acquired. On the other hand, when organic-ized clay exceeds the 200 weight sections, there is a possibility that distributing [ of clay ] may become inadequate. In addition, as for the upper limit of the amount of the above-mentioned organic-ized clay, considering as 30 weight sections is more desirable.

[0036] Moreover, in the resin composite material of this invention, when an elastomer above-mentioned block-copolymer type consists of a hard segment and a soft segment, it is desirable that 0.1-300 weight partial powder of the above-mentioned organic-ized clay is carried out to the 100 weight sections of the component which constitutes the above-mentioned hard segment. Thereby, thermal resistance can be raised and a creep property can be raised.

[0037] When organic-ized clay is under the 0.1 weight section, there are [ to restrain between hard segments enough but ] too few amounts of organic-ized clay, and there is a possibility that the effectiveness of this invention may no longer be acquired. On the other hand, when organic-ized clay exceeds the 300 weight sections, there is a possibility that distributing [ of clay ] may become inadequate. In addition, as for the minimum of the amount of the above-mentioned organic-ized clay, considering as 1 weight section is more desirable.

[0038] The resin composite material concerning this invention can be widely used as the same spring material as usual rubber. For example, it can be used, being able to process it into a hose ingredient, an isolator, the charge of an automatic in-the-car sheathing material, etc. Moreover, since it is processible like resin even if it has a property like rubber, it can be used as an injection-molding ingredient, an extrusion-molding ingredient, a press-forming ingredient, a blow molding ingredient, and a film material.

[0039] Next, as for the segment of the above-mentioned two or more classes, it is desirable like invention of claim 2 to become from the hard segment which has a functional group, and the soft segment which has a polar weak functional group rather than the functional group in which do not have a functional group or the above-mentioned hard segment has it.

[0040] In this case, a hard segment is a part which has a strong polar functional group. It is desirable to use what consists of a chain which consists of polystyrene, a polyamide, polyurethane, polyester, etc. so that it may mention later. The soft segment of another side is the part which does not have a functional group or had a weak polar functional group (polarity weaker than the functional group of the above-mentioned hard segment). It is desirable to use what consists of a chain which consists of polybutadiene, hydrogenation polybutadiene, polyisoprene, hydrogenation polyisoprene, a polyether, etc. so that it may mention later.

[0041] By using such an elastomer, the above-mentioned organic-ized clay is alternatively distributed to a hard segment. Thereby, a hard segment is restrained by clay and the bonding strength between hard segments increases. Moreover, clay does not distribute between soft segments. Thereby, the effectiveness of this invention can be acquired certainly. Furthermore, the thermal resistance of the resin composite material applied to this invention by the above-mentioned hard segment can be raised more, and the above-mentioned soft segment can raise more resiliency like the rubber of the resin composite material of this invention.

[0042] In addition, not all the organic-ized clay needs to distribute only to a hard segment, and even if it is in the condition that the part distributed to the soft segment, the effectiveness of this invention can be acquired.

[0043] Moreover, like invention according to claim 3, the above-mentioned hard segment is a chain which consists of at least one kind chosen from polystyrene, a polyamide, polyurethane, and polyester, and, as for the above-mentioned soft segment, it is desirable that it is the chain which consists of at least one kind chosen from polybutadiene, hydrogenation polybutadiene, polyisoprene, hydrogenation polyisoprene, and a polyether. Thereby, the effectiveness of this invention can be acquired much more certainly.

[0044]

[Embodiment of the Invention] About the resin composite material (samples 1-3) concerning the example of an

operation gestalt of example this invention of an operation gestalt, and its engine performance, it evaluates with the comparison samples C1 and C2. When the resin composite material of this example is explained briefly, as shown in drawing 1, these are in the condition that organic-ized clay 12 is distributed to one kind of segment 11 of block-copolymer type thermoplastic elastomer which consists of two or more kinds of segments 11 and 12.

[0045] The above-mentioned block-copolymer type thermoplastic elastomer is a polymer which has the segment which consists of two or more different molecule chains into 1 molecule, as shown in drawing 2. The so-called AB mold, the ABA mold, and the ABC mold were illustrated to drawing 2 (a), (b), and (c). In this drawing, Segment A, Segment B, and Segment C are chains different, respectively.

[0046] Next, each sample and a comparison sample are explained. The block-copolymer type thermoplastic elastomer which constitutes the resin composite material concerning a sample 1 is Hydrogenation SBS (hydrogenation polystyrene-polybutadiene-polystyrene) (a trade name, the tough tech H1013, Asahi Chemical make). This thing is matter which has the segment which consists of a segment which consists of polystyrene, and hydrogenation polybutadiene.

[0047] Organic-ized clay is Na-montmorillonite made organic by the octadecyl amine. In addition, Na-montmorillonite is a stratified clay mineral and has structure to which the laminating of many sheets was carried out.

[0048] The manufacture approach of a sample 1 is explained. First, 5000ml of 80-degree C water was made to distribute Na-montmorillonite 80g. Octadecyl amine 28.5g and 11ml of concentrated hydrochloric acid were dissolved in 2000ml of 80-degree C water, and this solution was added to previous montmorillonite dispersion liquid. The obtained precipitate was filtered and 80-degree C water washed 3 times. Then, the montmorillonite which was freeze-dried and was made organic with octadecyl ammonium was obtained. In addition, when a part for inorganic [ of the montmorillonite made / above-mentioned / organic by the \*\*\*\* method ] was measured, it was 68 % of the weight. Moreover, it was 22A when the distance between layers of the montmorillonite made [ above-mentioned ] organic according to the X diffraction was measured.

[0049] Such montmorillonite 38.4g made organic was supplied to the twin screw extruder with 400g of Hydrogenation SBS, and melting kneading of both was carried out. Kneading temperature was 200 degrees C and the axial rotational frequency was 200rpm. When asked for a part for inorganic [ of the resin which was extruded from the twin screw extruder and obtained ] by the \*\*\*\* method, it was 5 % of the weight. Moreover, when this resin was observed with the transmission electron microscope, as shown in drawing 1, it turned out that the montmorillonite is distributed in the shape of an island to resin to the order of nm (it turned out that there are a part currently distributed and a part which is not so).

[0050] Moreover, the temperature dependence of the elastic modulus of this resin was measured by dynamic viscoelasticity measurement. In addition, the programming rate at this time was considered as a part for 2-degree-C/. Organic-ized clay distributed this resin concerning a sample 1 very finely only in the specific part, and above showed further that the storage moduli in 90 degrees C of this resin were 13.0MPa(s).

[0051] Next, a sample 2 is explained. Montmorillonite 22.4g which was produced by the approach of a sample 1 and which was made organic was supplied to the twin screw extruder with hydrogenation SBS (the same tough tech H1013 as sample 1) 400g, and melting kneading of both was carried out. Kneading temperature was 200 degrees C and the axial rotational frequency was 200rpm. When asked for a part for inorganic [ of the resin which was extruded from the twin screw extruder and obtained ] by the \*\*\*\* method, it was 3 % of the weight.

[0052] Moreover, when this resin was investigated like the above, it turned out that the montmorillonite is distributed in the shape of an island to resin to the order of nm like a sample 1. Moreover, dynamic viscoelasticity measurement was performed for this resin like the above, and the temperature dependence of an elastic modulus was measured. In addition, the programming rate at this time was considered as a part for 2-degree-C/. Consequently, organic-ized clay distributed finely and this resin concerning a sample 2 was also found by that the storage moduli in 90 degrees C are 11.8MPa(s).

[0053] Next, the comparison sample C1 is explained. The comparison sample C1 is Hydrogenation SBS (the same tough tech H1013 as a sample 1). Dynamic viscoelasticity measurement was performed for this resin like the above, and the temperature dependence of an elastic modulus was measured. In addition, the programming rate at this time was considered as a part for 2-degree-C/. Consequently, it turned out that the storage moduli in 90 degrees C of this resin concerning the comparison sample C1 are 9.1MPa(s). As mentioned above, it turned out that the storage modulus in 90 degrees C is maintainable to a bigger value by distributing clay from a sample 1, a sample 2, and the comparison sample C1 to the specific segment (it becoming the part of polystyrene in this example) made organic.

[0054] In addition, the relation between the elastic modulus of a sample 1 and the comparison sample C1 and temperature was measured like the above to drawing 3, and was indicated to it. As found in this drawing, the



sample 1 and the comparison sample C1 have an elastic modulus with almost same low temperature - room temperature. As for the elastic modulus of the comparison sample C1, it turned out that it falls and ductility like bridge formation rubber is lost from the comparison sample C1 as temperature becomes high. On the other hand, it turned out that a sample 1 can maintain a higher elastic modulus in the temperature requirement of extent also used as an elevated temperature.

[0055] In addition, what was made into the condition that drawing 4 (b) which increased the quantity of and mentioned above the segment which consists of polystyrene by the approach of making [ many ] the rate of the styrene at the time of a polymerization, as a reference sample is started was prepared, the relation between an elastic modulus and temperature was measured also about this, and it indicated to this drawing. The elastic modulus of this thing was higher than the sample 1 and the comparison sample C1 in every temperature requirement (also setting to any of low temperature a room temperature - an elevated temperature). However, since the resin concerning this reference sample has the high elastic modulus at the time of a room temperature, compared with a sample 1, it becomes hard at the time of use, and the problem of being hard coming to deal with it tends to produce it.

[0056] Next, a sample 3 is explained. Montmorillonite 38.4g which was produced by the approach of a sample 1 and which was made organic was supplied to the twin screw extruder with urethane system elastomer (estrane C95A (product made from Takeda bar DISHU urethane industry)) 500g, and melting kneading of both was carried out. Kneading temperature was 200 degrees C and the axial rotational frequency was 200rpm. When asked for a part for inorganic [ of the resin which was extruded from the twin screw extruder and obtained ] by the \*\*\*\* method, it was 5 % of the weight.

[0057] In addition, the above-mentioned urethane system elastomer (estrane C95A (product made from the Takeda bar DISHU urethane industry)) is matter which has the segment which consists of polyurethane, and the segment which consists of a polyether.

[0058] Moreover, when this resin was investigated like the above, as a montmorillonite showed drawing 1 to resin to the order of nm, it turned out that it is distributed in the shape of an island. Moreover, dynamic viscoelasticity measurement was performed for this resin like the above, and the temperature dependence of an elastic modulus was measured. In addition, the programming rate at this time was considered as a part for 2-degree-C/. Consequently, it turned out that the storage moduli in 150 degrees C of this resin concerning a sample 3 are 10.1MPa(s).

[0059] Next, the comparison sample C2 is explained. The comparison sample C2 is an urethane system elastomer (the same estrane C95A as a sample 3). Dynamic viscoelasticity measurement was performed for this resin like the above, and the temperature dependence of an elastic modulus was measured. In addition, the programming rate at this time was considered as a part for 2-degree-C/. Consequently, it turned out that the storage moduli in 150 degrees C of this resin concerning the comparison sample C2 are 7.2MPa(s).

[0060] As mentioned above, the sample 3 and the comparison sample C2 showed that the storage modulus in 150 degrees C was maintainable to a bigger value by making the segment which consists of polyurethane of block-copolymer type thermoplastic elastomer called an urethane system elastomer distribute the clay made organic.

[0061] The operation effectiveness of this example is explained below. Each resin composite material concerning the sample 1 concerning this example - a sample 3 is in the condition that the montmorillonite made organic distributed to one segment of block-copolymer type thermoplastic elastomer which consists of two segments.

[0062] A montmorillonite is a clay mineral and has the layer structure to which many sheets of silicate were also piled up. As the montmorillonite and the above-mentioned elastomer which were made organic were mentioned above, the strong polar segment (samples 1 and 2 polystyrene and a sample 3 polyurethane) in an elastomer intercalates between the sheets which constitute the layer structure of a montmorillonite by carrying out melting kneading with a twin screw extruder, and the sheet of a laminating condition is mostly put in order as a condition of a monolayer.

[0063] The sheet of the montmorillonite which became scatteringly restraining each segment by this, the role which combines each segment mutually will be played, whenever it is shown in drawing 1, it will come, and it will produce and cheat out of the structure also similar to the point of bridge formation rubber constructing a bridge inside resin composite material.

[0064] By the above, the sample 1 concerning this example - a sample 3 can demonstrate the pliant elasticity just like bridge formation rubber, and further, since its force in which the sheet of a montmorillonite restrains each segment is quite strong, as shown in drawing 3, they can prevent decline in the elastic modulus in higher temperature. That is, the thermal resistance of resin composite material can be raised.

[0065]



[Effect of the Invention] As mentioned above, according to this invention, it excels in thermal resistance and the resin composite material which has pliant resiliency like bridge formation rubber also in ordinary temperature can be offered.

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[Translation done.]

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CLAIMS

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[Claim(s)]

[Claim 1] Resin composite material characterized by organic-ized clay distributing to at least one kind of segment of block-copolymer type thermoplastic elastomer which consists of two or more kinds of segments.

[Claim 2] It is the resin composite material characterized by becoming from the soft segment which has a polar weak functional group rather than the functional group in which the segment of the above-mentioned two or more classes does not have the hard segment which has a functional group, and a functional group in claim 1, or the above-mentioned hard segment has.

[Claim 3] It is the resin composite material characterized by for the above-mentioned hard segment being a chain which consists of at least one kind chosen from polystyrene, a polyamide, polyurethane, and polyester in claim 2, and the above-mentioned soft segment being a chain which consists of at least one kind chosen from polybutadiene, hydrogenation polybutadiene, polyisoprene, hydrogenation polyisoprene, and a polyether.

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[Translation done.]

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